

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE FEB 06 2002 INTERNATIONAL APPLICATION NO. DE00/02661		ATTORNEY'S DOCKET NUMBER 266-01US U.S. APPLICATION NO. (If known, see 37 CFR 1.5 10/049482
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		PRIORITY DATE CLAIMED 8/6/1999
TITLE OF INVENTION Thermoplastic Polymer Blend Produced from Thermoplastic Starch and Method for the Production Thereof		
APPLICANT(S) FOR DO/EO/US Werner Berger, Lutz Jeromin, and Guntram Opitz		
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:		
<p>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</p> <p>2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</p> <p>3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.</p> <p>4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31).</p> <p>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))</p> <p>a. <input type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau).</p> <p>b. <input checked="" type="checkbox"/> has been communicated by the International Bureau.</p> <p>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</p> <p>6. <input type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2))</p> <p>a. <input type="checkbox"/> is attached hereto.</p> <p>b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4).</p> <p>7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))</p> <p>a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau).</p> <p>b. <input type="checkbox"/> have been communicated by the International Bureau.</p> <p>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</p> <p>d. <input type="checkbox"/> have not been made and will not be made.</p> <p>8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</p> <p>9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).</p> <p>10. <input type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</p>		
<p><b>Items 11 to 20 below concern document(s) or information included:</b></p> <p>11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</p> <p>12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</p> <p>13. <input type="checkbox"/> A <b>FIRST</b> preliminary amendment.</p> <p>14. <input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.</p> <p>15. <input type="checkbox"/> A substitute specification.</p> <p>16. <input type="checkbox"/> A change of power of attorney and/or address letter.</p> <p>17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.</p> <p>18. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4).</p> <p>19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).</p> <p>20. <input checked="" type="checkbox"/> Other items or information: Application Data Sheet</p>		
<p>"Express Mail" Label # EU 092 122 855 US - I hereby certify that this paper or fee is being deposited with the USPS "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on 2/6/2002, and is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231. <i>Gudrun E. Huckett</i> Gudrun E. Huckett, Patent Agent</p>		

U.S. APPLICATION NO. (if known, see 37 CFR 1.50)	INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUMBER		
<b>10/049482</b>	<b>PCT/DE00/02661</b>	<b>266-01US</b>		
21. <input checked="" type="checkbox"/> The following fees are submitted:		<b>CALCULATIONS PTO USE ONLY</b>		
<b>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):</b>				
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO .....		<b>\$1040.00</b>		
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO .....		<b>\$890.00</b>		
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO .....		<b>\$740.00</b>		
International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) .....		<b>\$710.00</b>		
International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) .....		<b>\$100.00</b>		
<b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>		<b>\$ 890.00</b>		
Surcharge of <b>\$130.00</b> for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).		<b>\$ 130.00</b>		
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$
Total claims	21 - 20 =	1	x \$18.00	\$ 18.00
Independent claims	3 - 3 =	0	x \$84.00	\$
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$280.00	\$ 280.00
<b>TOTAL OF ABOVE CALCULATIONS =</b>		<b>\$ 1318.00</b>		
<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.		<b>\$ 659.00</b>		
		<b>SUBTOTAL = \$ 659.00</b>		
Processing fee of <b>\$130.00</b> for furnishing the English translation later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).		<b>\$ 130.00</b>		
<b>TOTAL NATIONAL FEE =</b>		<b>\$ 789.00</b>		
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). <b>\$40.00</b> per property +		\$		
<b>TOTAL FEES ENCLOSED =</b>		<b>\$ 789.00</b>		
		<b>Amount to be refunded:</b>		\$
		<b>charged:</b>		\$
<p>a. <input checked="" type="checkbox"/> A check in the amount of <b>\$ 789.00</b> to cover the above fees is enclosed. <b>check # 1341</b></p> <p>b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of <b>\$ _____</b> to cover the above fees. A duplicate copy of this sheet is enclosed.</p> <p>c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <b>50-1199</b>. A duplicate copy of this sheet is enclosed.</p> <p>d. <input type="checkbox"/> Fees are to be charged to a credit card. <b>WARNING: Information on this form may become public. Credit card information should not be included on this form.</b> Provide credit card information and authorization on PTO-2038.</p>				
<p><b>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.</b></p> <p>SEND ALL CORRESPONDENCE TO:</p> <p><b>Gudrun E. Huckett, Patent Agent P.O. Box 3187 Albuquerque, NM 87190-3187</b></p>				
<p><u>Gudrun E. Huckett</u> SIGNATURE <b>Gudrun E. Huckett</b></p> <p>NAME <b>35,747</b></p> <p>REGISTRATION NUMBER <b>2/6/2002</b></p>				

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CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
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MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ <b>\$280.00</b> <b>\$ 280.00</b>
<b>TOTAL OF ABOVE CALCULATIONS</b>			<b>\$ 1318.00</b>
<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2. <b>\$ 659.00</b>			
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SEND ALL CORRESPONDENCE TO:			
<p style="text-align: right;"><u>Gudrun E. Huckett</u></p> <p style="text-align: right;">SIGNATURE</p> <p style="text-align: right;">Gudrun E. Huckett</p>			
<p>Gudrun E. Huckett, Patent Agent P.O. Box 3187 Albuquerque, NM 87190-3187</p>			
<p>NAME <b>35,747</b></p>			
<p>REGISTRATION NUMBER <b>2/6/2002</b></p>			

10049432

## Thermoplastic Polymer Blend Produced From Thermoplastic Starch and Method for the Production Thereof

The invention relates to a thermoplastic polymer blend comprising thermoplastic starch as well as a method for producing a thermoplastically deformable, biologically degradable polymer blend, that is shape-resistant in water, on the basis of native starch, synthetic polymers, for example, aliphatic polyesters and their copolymers, polyvinyl acetate (PVAc), polyvinyl alcohol (PVOH) and other, preferably biologically degradable synthetic polymers with addition of a hydrolysis component on the basis of PVAc as well as water or/and lower polyfunctional alcohols by reactive extrusion, preferably in double screw extruders. The reaction product can be processed as a function of the product composition by means of conventional processing machines for thermoplastics to injection molded, deep-drawn, and blow molded parts as well as foils with adjustable service value properties, for example, shape resistance in water and biological degradability. The polymer blend according to the invention is also used as a raw material for fibers as well as material for melt film coatings.

In recent years, several methods for manufacturing and forming thermoplastic starch (TPS), alone or in the form of a polymer mixture or polymer melt or polymer blend, have become known. This research has been carried out with the goal of making available new or broader fields of application for renewable raw materials.

It is known to hydrolyze the grainy structure of native starch first with defined proportions of water or/and lower polyfunctional alcohols, such as ethylene glycol, propylene glycol, glycerol, 1,3-butanediol, diglyceride, corresponding ethers, but also components such as dimethylsulfoxide, dimethylformamide, dimethylurea, dimethyl acetamide and/or other additives to a thermoplastic material by thermo-mechanical hydrolysis in conventional double screw extruders.

process with intensive mixing action. Optionally, acetic acid is added in order to neutralize not yet reacted water glass after saponification of PVAc with water glass. It was found that already minimal additions of this component results in a significant quality improvement of the extruded material and of the products produced thereof.

5 Significantly more native starch can be used in comparison to the prior art without discoloration or with only minimal discoloration while maintaining or improving the shape resistance in water. Apparently, the component contributes to making the two phases, i.e., the hydrophilic thermoplastic starch and the hydrophobic polymer which, in fact, are immiscible, miscible to a certain degree.

10 Further experiments have shown that the quality of the end product with respect to shape stability in water and strength must be improved even further. In particular, it was impossible to produce thin foils under approximately 300 µm thickness.

15 It has already been suggested (DE 197 50 846) to produce a component of polyvinyl acetate and alkali water glass and to extrude this component together with starch and a hydrophobic polymer, for example, polyvinyl acetate, to a high-quality polymer mixture. For producing the component, polyvinyl acetate was saponified to a hydrolyzation degree of up to 90 % in the presence of catalytic amounts of low-molecular organic mono-, di- and trihydroxy components (for example, methanol, ethanol, ethylene glycol, glycerin) and with continuous addition of alkaline-reacting 20 components and of the alkali silicate in a batch process.

25 It was found that with this component, which obviously acts as a compatibility agent, polymer mixtures with high starch proportions can be extruded in analogy to DE 195 33 800. The products produced of this polymer mixtures have a significantly greater quality in regard to several parameters. In particular, foils of a thickness of less than 100 µm can be produced.

in the mixture. A prior energy-intensive drying is not required. Moreover, it was found that the addition of the catalyst allows adjustment of the rheologic properties of the mixture within certain limits. Accordingly, the adjustment of the viscosity of the polymers can be improved. It is possible to adjust excellent reproducible processing

5 conditions within the extruder.

With the processing conditions according to the invention, it is possible to adjust a bi-continuous phase morphology of the system and to keep it stable. Fig. 1 shows a microscope image (phase contrast microscope) of TPS-Bionolle blends produced according to the invention. The bi-continuity of the dark and light phases which

10 remains stable can be seen.

The bi-continuous phase morphology of the polymer blend according to the invention has a broader variety in regard to the property profile (for example, greater proportions of starch, improved biological degradability, adjustment of the permeation properties) than systems with insular/matrix structures (see L. A. Utracki, *Polymer Alloys and*

15 *Blends: Thermodynamics and Theology*, Munich, Vienna, New York, Hanser Publishers 1989 or *Handbuch der technischen Polymerchemie*, VCH Verlag Chemie, Weinheim, New York, Basel, Cambridge, Tokyo). Transparent films are possible with very fine dispersions (particle diameters < 100 nm) with which an expansive phase separation does not occur. The bi-continuous phase structure has also the advantage that the hydrophobic properties of the synthetic polymer component even for a relatively minimal proportion within the total mixture are imparted to the material as a whole. At the same time, the properties of the thermoplastic starch, such as high mechanical strength, minimal oxygen permeability, quick biological degradability, remain intact.

20 25 A PVAc component which has been partially saponified to a saponification degree of

1	TPS	13.2
2	TPS + catalyst (0.1 % HNO <sub>3</sub> )	4.0
3	TPS + catalyst (0.15 % HNO <sub>3</sub> )	1.4
4	TPS + partially saponified PVAc (appr. 1:1)	24.9
5	TPS + partially saponified PVAc (appr. 1:1) + catalyst (0.1 % HNO <sub>3</sub> )	25.2
6	TPS + partially saponified PVAc + Bionolle (appr. 1/3 : 1/3 : 1/3) + catalyst (0.1 % HNO <sub>3</sub> )	23.7
7	native potato starch	40
8	MaterBi	0.4

10 As can be easily seen when comparing the values 1, 2 and 3, the catalyst has a negative effect on the molecular weight. It decreases the molecular weight of TPS greatly. On the other hand, the values 1 and 4 show that the hydrolysis component on PVAc basis increases the molecular weight in the mixture with TPS. In this mixture, the acidic catalyst no longer reduces the molecular weight (value 5). Apparently, the  
15 hydrolyzed component acts as a compatibility agent. An effect which must be based on the particular properties of the hydrolyzed component because the molecular weight is not further increased by addition of an additional further synthetic component, for example, Bionolle (aliphatic co-polyester produced by the company Showa Denko, poly (butylene succinate-co-adipate) (value 6). In the combination with the  
20 compatibility agent the above-mentioned advantageous effects of the acidic catalyst can be employed without disadvantages regarding a too great reduction of the molecular weight. As will be demonstrated in the following by means of examples, the foils extruded from the polymer mixtures have excellent strength values. When comparing the values, in particular 2, 4, and 5, a synergistic effect can even be seen  
25 in regard to the acidic catalyst and the compatibility agent.

As a polymer component different aliphatic polyesters and their copolymers, polyvinyl

All examples have in common that native starch with 16 to 20 % moisture content and the hydrolyzed component together with approximately 1 % stearic acid and silica gel, respectively, are mixed in a quick mixing device to an easy-flowing powder mixture. This powder mixture, and Bionolle as well as glycerin via separate metering devices, 5 is introduced into a double screw extruder with tightly meshing screws rotating in the same direction (manufacturer: Berstorff ZE25, L/D = 32). The total mass throughput is 2.5 kg per hour. The temperature profile along the extrusion stretch ensures that the extruded material is heated by thermal and mechanical energy introduction to at least 180°C and is subsequently cooled. The extruded material exits from the extruder 10 through a round strand nozzle at a temperature of approximately 100°C and, after a subsequent cooling by air, can be granulated. The granular material has a residual moisture contents, required for further processing, of 6-10 % by weight (gravimetric determination, infrared drying at 120°C, 15 minutes drying time).

The granular material is suitable for further processing to tubular film. For this purpose, 15 it is re-extruded with the above-mentioned extruder at a maximum cylinder temperature of 130°C and is then shaped by an annular nozzle (diameter of 25 mm) to a tubular shape. The tubular shape is then blown to two to three times its diameter. Moreover, two examples with drawn sheet foils are provided in the table for comparison.

The quality of the starch polymer blend is determined with regard to resistance to water 20 and tensile strength according to the following procedures.

Strand samples of approximately 2 cm length are stored 24 hours in water at room temperature; subsequently, the surface water is removed with filter paper and the samples are weighed for determining the water absorption property (moisture expansion). These samples are dried subsequently for 8 hours at 90°C in a heating 25 chamber and are weighed. Taking into consideration the moisture content of the

original samples, which has been determined on simultaneously dried comparative examples free of moisture expansion, the mass loss and the product proportion soluble in cold water can be determined.

5 For the tensile tests, specimens in the form of a dumbbell are stamped out of the foil in the extrusion direction and are conditioned 48 hours in an atmosphere which will be generated in a closed container above an 80 % glycerin/water mixture at room temperature.

10 The tensile test is carried out with a ZWICK - Universalprüfmaschine (ZWICKI 1120) in accordance with DIN 53 455. The tensile stress at break, stretch at break, and the modulus of elasticity are employed for evaluation purposes.

The hydrolyzed component is produced by saponification of an aqueous polyvinyl acetate dispersion with NaOH at 120 - 140°C.

15 To the mixture 12.5 % glycerin, relative to the total weight, are added. The percentages of the component and of Bionolle are provided in the following table. The values are based on 100 % by weight of the mixture without glycerin. The proportion of the native starch is calculated based on the difference to 100 % (also without glycerin).

20 The table shows that foils with a reduced thickness (approximately 30 µm) can be produced. In all examples it was found that the processing properties had been improved significantly. The mechanical properties of the foils, increased tensile strength, stretching ability, etc., are significantly improved.

According to a further embodiment, native starch, glycerin as a plasticizer for the

starch, the hydrolysis component on PVAc basis, and a starch acetate/PEG blend Sconacell A in the presence with addition of an acidic catalyst ( $\text{HNO}_3$ ) were extruded by means of a double screw extruder with screws rotating in the same direction. The obtained polymer blend was re-extruded and processed to a tube film.

5 In the following table the properties of the produced tube film, one produced with and one produced without catalyst addition, are illustrated.

Ex.	Compatibility Agent (%)	Sconacell A (%)	catalyst	catalyst proportion (%)	thickness ( $\mu\text{m}$ )	$\rho_{\text{max}}$ (MPa)	$\varepsilon_{\text{max}}$ (%)	tensile module (MPa)
15	33.5	30	-	-	80-110	11.1	10	1323
16	33.5	30	$\text{HNO}_3$	0.1	60-80	14.9	7	1530

10 It is demonstrated that the tensile strengths of the films are increased when an acidic catalyst is added in the first extrusion step.

Table with Various Examples

Examples	Compatibility Agent (%)	Bionolle #3001 [%]	catalyst	proportion [%]	foil thickness [µm]	$\rho_{\max}$ (MPa)	$\xi_{\text{peak}}$ [%]	tensile module (MPa)
1 (sheet foil)	---	30	---	0	200-300	8.7	55	128
2	---	30	---	0	70-120	9.4	61	74
3 (sheet foil)	---	30	TPP	1	200-300	8.6	71	95
4	---	30	TPP	1	70-100	12.0	23	301
5	33.5	30	---	0	30-90	14.5	130	174
6	33.5	30	TPP	1	45-60	18.4	167	293
7	33.5	30	Tyzor TOT	1	30-40	17.0	102	119
8	33.5	30	HNO <sub>3</sub>	0.1	40-50	21.1	120	248
9	33.5	30	H <sub>2</sub> SO <sub>4</sub>	0.2	50-90	17.4	121	218
10	33.5	30	HCl	0.2	30-60	16.6	124	251
11	33.5	30	p-TSS	0.1	40-60	21.4	119	367
12	33.5	30	HNO <sub>3</sub>	0.1	40-50	19.7	110	259
13	27.5	30	HNO <sub>3</sub>	0.1	35-45	19.9	83	322
14	30	25	HNO <sub>3</sub>	0.1	35-50	20.5	67	336

TPP ... triphenyl phosphite  
 Tyzor TOT ... tetra-2-ethylhexyl titanate  
 p-TSS ... p-toluene sulfonic acid

## Claims

1. Thermoplastic polymer blend comprising a bi-continuous phase structure of thermoplastic starch, at least one synthetic polymer, and a hydrolysis component on PVAc basis, wherein the starch component of the polymer blend has a molecular weight which is only minimally reduced relative to native starch.
2. Thermoplastic polymer blend according to claim 1, characterized in that it contains moreover extending agents, filling agents, internal lubricants, flow-improving agents, dyes, pigments, or mixtures thereof.
3. Thermoplastic polymer blend according to claim 1 or 2, characterized in that, relative to the total composition, it comprises 30-70 % by weight thermoplastic starch, 20-40 % by weight synthetic polymer, and 6-25 % by weight hydrolysis component on PVAc basis, and optionally an acidic catalyst component.
4. Thermoplastic polymer blend according to claim 1, wherein the synthetic polymer is a biologically degradable aliphatic polyester or their copolymers or polyvinyl acetate or their copolymers or a water-resistant starch derivative or cellulose derivative or polyvinyl alcohol or their copolymers or a water-resistant starch or cellulose derivative.
5. Method for producing a thermoplastic polymer blend by reactive extrusion of a mixture of native starch and at least one hydrophobic polymer with addition of a hydrolyzed component on polyvinyl acetate basis and of low polyfunctional alcohols or/and water, characterized in that the mixture is extruded in the presence of an acidic catalyst.
6. Method according to claim 5, characterized in that the acidic catalyst is an organometallic compound, such as dibutyl tin oxide, dibutyl tin dilaurate, tetra-2-

ethylhexyl titanate, triethanolamine zirkonate, titanate compound chelated with lactic acid, triethanolamine titanate or/and alkyl titanate.

7. Method according to claim 5, characterized in that the acidic catalyst is a Lewis acid (such as, for example, triphenyl phosphite).

5 8. Method according to claim 6 or 7, characterized in that the mixture comprises 0.5 % to 2 % of the acidic catalyst, relative to its total weight.

9. Method according to claim 5, characterized in that the acidic catalyst is an acid, such as nitric acid, sulfuric acid, hydrochloric acid or/and p-toluene sulfonic acid.

10 10. Method according to claim 9, characterized in that the mixture comprises 0.05 to 0.2 % of the acidic catalyst, relative to its total weight.

11. Method according to claim 5, characterized in that, for producing the hydrolyzed component, the polyvinyl acetate is saponified to a hydrolysis degree of 20 to 70 %.

15 12. Method according to claim 11, characterized in that the polyvinyl acetate is saponified to a hydrolysis degree of 30 % to 55 %.

13. Method according to claim 11, characterized in that an aqueous polyvinyl acetate dispersion is saponified at 120 - 140 °C with sodium hydroxide solution.

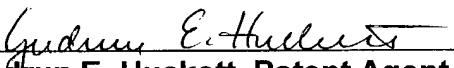
20 14. Method according to claim 11, characterized in that the hydrolyzed component on polyvinyl acetate basis is adjusted to a residual moisture contents of 15 - 35 %.

15. Method according to claim 5, characterized in that the native starch, the hydrolyzed component on polyvinyl acetate basis, and the catalyst are mixed to a well-flowing powder mixture.
16. Method according to claim 15, characterized in that approximately 1 % stearic acid, relative to its total weight, is added to the powder mixture.
17. Method according to claim 15, characterized in that approximately 1 % silica gel, relative to its total weight, is added to the powder mixture.
18. Method according to claim 11, characterized in that the catalyst is metered in a liquid state mixed with glycerin.
- 10 19. Use of a thermoplastic polymer blend according to one of the claims 1 to 18, respectively, for producing injection molded, deep-drawn, or blow-molded parts, foils or raw materials for fibers as well as material for melt film coatings.

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

**Certificate of Mailing**

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**Gudrun E. Huckett, Patent Agent**

Applicant: Werner Berger, et al.  
Serial No: 10/049,482 (based on PCT/DE00/02661)  
International Filing Date: 8/5/2000  
National Stage Entered: 2/6/2002  
Title: Thermoplastic Polymer Blend Produced From Thermoplastic Starch and Method for the Production Thereof

**Assistant Commissioner for Patents**

**Washington, D.C. 20231**

**PRELIMINARY AMENDMENT**

Prior to the first office action, please amend the instant application as follows:

**IN THE SPECIFICATION:**

Please substitute the attached clean copies of the amended paragraphs of pages 1, 4, and 8 for the corresponding paragraphs on file. A marked-up version of the paragraphs with all the changes shown is also attached.

**IN THE CLAIMS:**

Claims 1 through 19 of the literal translation are cancelled.

Please add the attached new claims 20 through 39 to the specification.

IN THE ABSTRACT:

Please add the attached Abstract of the Disclosure to the specification.

REMARKS

Claims 1-19 of the literal translation have been cancelled and replaced with claims 20-39 drafted in proper U.S. format. Proper headings according to the guidelines for drafting a nonprovisional patent application under 35 U.S.C. 111(a) have been added. A proper Abstract of the Disclosure has been added to the specification.

In view of the foregoing, it is submitted that this application is now in condition for allowance and such allowance is respectfully solicited.

Authorization is herewith given to charge any fees or any shortages in any fees required during prosecution of this application and not paid by other means to Patent and Trademark Office deposit account 50-1199.

Respectfully submitted on July 24, 2002

*Gudrun E. Huckett*  
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GEH

Encl.

- new claims 20-39 (3 sheets);
- amended paragraphs of pages 1, 4, 8 (clean copies and marked-up versions; 6 sheets);
- Abstract of the Disclosure (1 sheet)

## NEW CLAIMS 20-39

20. A thermoplastic polymer blend comprising a thermoplastic starch, at least one synthetic polymer, and a hydrolysis component on PVAc basis, wherein the starch component of the polymer blend has a molecular weight which is only minimally reduced relative to native starch, wherein the thermoplastic polymer blend has a bi-continuous phase structure.

21. The thermoplastic polymer blend according to claim 20, comprising extending agents, filling agents, internal lubricants, flow-improving agents, dyes, pigments, or mixtures thereof.

22. The thermoplastic polymer blend according to claim 20, comprising, relative to the total composition of the polymer blend, 30-70 % by weight of the thermoplastic starch, 20-40 % by weight of the synthetic polymer, and 6-25 % by weight of the hydrolysis component on PVAc basis.

23. The thermoplastic polymer blend according to claim 22, further comprising an acidic catalyst component.

24. The thermoplastic polymer blend according to claim 20, wherein the synthetic polymer is a biologically degradable aliphatic polyester or a polyester copolymer or polyvinyl acetate or a polyvinyl acetate copolymer or a water-resistant starch derivative or a water-resistant cellulose derivative or polyvinyl alcohol or a polyvinyl alcohol copolymer.

25. A method for producing a thermoplastic polymer blend by reactive extrusion, the method comprising the steps of:

a) mixing native starch, at least one hydrophobic polymer, a hydrolyzed component on polyvinyl acetate basis, and at least one of lower polyfunctional alcohols and water; and

b) adding an acidic catalyst to the mixture of step a) and extruding the mixture in the presence of the acidic catalyst.

26. The method according to claim 25, wherein the acidic catalyst is an organometallic compound selected from the group consisting of dibutyl tin oxide, dibutyl

39. The method according to claim 32, wherein the acidic catalyst is metered in a liquid state mixed with glycerin.

## **CLEAN COPY OF AMENDED 1ST PARAGRAPH OF PAGE 1**

### **BACKGROUND OF THE INVENTION**

#### **1. Field of the Invention**

The invention relates to a thermoplastic polymer blend comprising thermoplastic starch as well as a method for producing a thermoplastically deformable, biologically degradable polymer blend, that is shape-resistant in water, on the basis of native starch, synthetic polymers, for example, aliphatic polyesters and their copolymers, polyvinyl acetate (PVAc), polyvinyl alcohol (PVOH) and other, preferably biologically degradable synthetic polymers with addition of a hydrolysis component on the basis of PVAc as well as water or/and lower polyfunctional alcohols by reactive extrusion, preferably in double screw extruders. The reaction product can be processed as a function of the product composition by means of conventional processing machines for thermoplastics to injection molded, deep-drawn, and blow molded parts as well as foils with adjustable service value properties, for example, shape resistance in water and biological degradability. The polymer blend according to the invention is also used as a raw material for fibers as well as material for melt film coatings.

#### **2. Description of the Related Art**

**CLEAN COPY OF AMENDED 1ST PARAGRAPH OF PAGE 4**

**SUMMARY OF THE INVENTION**

Based on the ecological goals of employing renewable raw materials to an even greater extent and to economically produce environmentally safe products, it is an object of the invention to provide a polymer blend on the basis of thermoplastic starch with improved properties.

### DESCRIPTION OF PREFERRED EMBODIMENTS

The invention will be explained in the following with the aid of several examples.

**MARKED-UP VERSION OF 1ST PARAGRAPH OF PAGE 1**

**BACKGROUND OF THE INVENTION**

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The invention relates to a thermoplastic polymer blend comprising thermoplastic starch as well as a method for producing a thermoplastically deformable, biologically degradable polymer blend, that is shape-resistant in water, on the basis of native starch, synthetic polymers, for example, aliphatic polyesters and their copolymers, polyvinyl acetate (PVAc), polyvinyl alcohol (PVOH) and other, preferably biologically degradable synthetic polymers with addition of a hydrolysis component on the basis of PVAc as well as water or/and lower polyfunctional alcohols by reactive extrusion, preferably in double screw extruders. The reaction product can be processed as a function of the product composition by means of conventional processing machines for thermoplastics to injection molded, deep-drawn, and blow molded parts as well as foils with adjustable service value properties, for example, shape resistance in water and biological degradability. The polymer blend according to the invention is also used as a raw material for fibers as well as material for melt film coatings.

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**MARKED-UP VERSION OF 1ST PARAGRAPH OF PAGE 4**

**SUMMARY OF THE INVENTION**

Based on the ecological goals of employing renewable raw materials to an even greater extent and to economically produce environmentally safe products, it is an object of the invention to provide a polymer blend on the basis of thermoplastic starch with improved properties.

**MARKED-UP VERSION OF 5TH FULL PARAGRAPH OF PAGE 8**

**DESCRIPTION OF PREFERRED EMBODIMENTS**

The invention will be explained in the following with the aid of several examples.

## ABSTRACT OF THE DISCLOSURE

A thermoplastic polymer blend of a bi-continuous phase structure contains thermoplastic starch, at least one synthetic polymer, and a hydrolysis component on PVAc basis. The starch component of the polymer blend has a molecular weight which is only minimally reduced relative to native starch. The thermoplastic polymer blend is produced by reactive extrusion of a mixture of native starch and at least one hydrophobic polymer with addition of a hydrolyzed component on polyvinyl acetate basis and of lower polyfunctional alcohols and water in the presence of an acidic catalyst. The thermoplastic polymer blend is used for producing injection molded, deep-drawn, or blow-molded parts, foils or raw materials for fibers as well as material for melt film coatings.

Docket No.: 266-01US

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Gudrun E. Huckett  
Gudrun E. Huckett, Patent Agent

In the application of: Werner Berger, et al.  
Serial Number: 10/049,482 (based on PCT/DE00/02661)  
International Filing Date: 8/5/2000  
National Stage Entered: 2/6/2002  
Title: Thermoplastic Polymer Blend Produced From Thermoplastic  
Starch and Method for the Production Thereof

**Assistant Commissioner for Patents  
BOX PCT  
Washington, D.C. 20231**

**LETTER IN RESPONSE TO NOTIFICATION OF MISSING REQUIREMENTS**

DATED 4/25/02

A missing parts notification dated 4/25/02 (copy enclosed) was mailed to the undersigned. In response to this notice, applicant submits the required oath/declaration.

The required fees have been paid at the time of entry of the national stage.

Also enclosed is a translation of the international application and a preliminary amendment to bring the translation into proper form according to U.S. patent practice. The attached translation is accurate. It is respectfully requested that the attached translation be used for prosecution purposes.

Authorization is herewith given to charge any fees or any shortages in any fees required during prosecution of this application and not paid by other means to Patent and Trademark Office deposit account 50-1199.

Respectfully submitted on July 24, 2002,



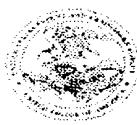
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Encl.: copy of missing parts letter; declaration; petition for time extension



## UNITED STATES PATENT AND TRADEMARK OFFICE

Commissioner for Patents, Box 9001  
United States Patent and Trademark Office  
Washington, D.C. 20591  
www.uspto.gov

U.S. APPLICATION NUMBER NO.	FIRST NAMED APPLICANT	ATTY. DOCKET NO.
10/049,482	Werner Berger	266-01US
INTERNATIONAL APPLICATION NO.		PCT/DE00/02661
I.A. FILING DATE		PRIORITY DATE
08/05/2000		08/06/1999
<b>CONFIRMATION NO. 3990</b> <b>371 FORMALITIES LETTER</b>  *OC000000007938032*		

Date Mailed: 04/25/2002

**NOTIFICATION OF MISSING REQUIREMENTS UNDER 35 U.S.C. 371 IN THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US)**

The following items have been submitted by the applicant or the IB to the United States Patent and Trademark Office as a Designated Office (37 CFR 1.494):

- U.S. Basic National Fees
- Priority Document
- Copy of IPE Report
- Copy of references cited in ISR
- Copy of the International Application
- Copy of the International Search Report
- Request for Immediate Examination
- Small Entity Statement

The following items **MUST** be furnished within the period set forth below in order to complete the requirements for acceptance under 35 U.S.C. 371:

- Oath or declaration of the inventors, in compliance with 37 CFR 1.497(a) and (b), identifying the application by the International application number and international filing date.

**ALL OF THE ITEMS SET FORTH ABOVE MUST BE SUBMITTED WITHIN TWO (2) MONTH FROM THE DATE OF THIS NOTICE OR BY 22 or 32 MONTHS (where 37 CFR 1.495 applies) FROM THE PRIORITY DATE FOR THE APPLICATION, WHICHEVER IS LATER. FAILURE TO PROPERLY RESPOND WILL RESULT IN ABANDONMENT.**

The time period set above may be extended by filing a petition and fee for extension of time under the provisions of 37 CFR 1.136(a).

Applicant is reminded that any communications to the United States Patent and Trademark Office must be mailed to the address given in the heading and include the U.S. application no. shown above (37 CFR 1.5)

*A copy of this notice **MUST** be returned with the response.*

DEBORAH D WILLIAMS

Telephone: (703) 305-3744

**PART 1 - ATTORNEY/APPLICANT COPY**

U.S. APPLICATION NUMBER NO.	INTERNATIONAL APPLICATION NO.	ATTY. DOCKET NO.
10/049,482	PCT/DE00/02661	266-01US



FORM PCT/DO/EO/905 (371 Formalities Notice)

## **Thermoplastisches Polymer-Blend aus thermoplastischer Stärke sowie Verfahren zu deren Herstellung**

Die Erfindung betrifft ein thermoplastisches Polymer-Blend aus thermoplastischer Stärke sowie ein Verfahren zur Herstellung eines thermoplastisch verformbaren, wasserformbeständigen, biologisch abbaubaren Polymerblends auf der Basis von nativer Stärke, synthetischen Polymeren, wie z. B. aliphatische Polyester, und deren Copolymeren, Polyvinylacetat (PVAc), Polyvinylalkohol (PVOH) und anderen, vorzugsweise biologisch abbaubaren synthetischen Polymeren unter Zusatz einer Hydrolysekomponente auf PVAc-Basis sowie von Wasser oder/und niederen polyfunktionellen Alkoholen durch reaktive Extrusion, vorzugsweise in Doppelwellenextrudern. Das Reaktionsprodukt kann in Abhängigkeit von der Produktzusammensetzung auf konventionellen Thermoplast-Verarbeitungsmaschinen zu Spritzguß-, Tiefzieh- und Blasformteilen sowie Folien mit einstellbaren Gebrauchswerteigenschaften, z. B. Wasserformbeständigkeit und biologische Abbaubarkeit, verarbeitet werden. Das erfindungsgemäße Polymer-Blend wird auch für Faserrohstoffe sowie als Material für Schmelzebeschichtungen verwendet.

In den letzten Jahren sind zahlreiche Verfahren zur Herstellung und Verformung von thermoplastischer Stärke (TPS) allein oder in einer Polymermischung bzw. Polymerschmelze oder Polymerblend bekannt geworden. Diese Arbeiten wurden mit dem Ziel ausgeführt, neue bzw. erweiterte Einsatzfelder für nachwachsende Rohstoffe zu erschließen.

Es ist bekannt, die körnige Struktur nativer Stärke zuerst mit definierten Anteilen an Wasser oder/und niederen polyfunktionellen Alkoholen, wie Ethylenglykol, Propylenglykol, Glycerol, 1,3-Butandiol, Diglycerid, entsprechende Ether, aber auch Verbindungen wie Dimethylsulfoxid, Dimethylformamid, Dimethylharnstoff, Dimethylacetamid und/oder anderen Zusatzstoffen durch einen thermomechanischen Aufschluß zu thermoplastischem Material mit Hilfe von konventionellen Doppelwellenextrudern aufzuschließen.

Verbesserung der Wasserformbeständigkeit kann gegenüber dem Stand der Technik erheblich mehr native Stärke eingesetzt werden. Offensichtlich trägt die Komponente dazu bei, daß die beiden an sich mischungsunverträglichen Phasen, die hydrophile thermoplastische Stärke und das hydrophobe Polymer, bis zu einem gewissen Grad mischbar werden.

Weitere Versuche haben gezeigt, daß die Qualität der Endprodukte hinsichtlich der Wasserformbeständigkeit und Festigkeit noch weiter verbessert werden muß. Insbesondere war es auch nicht möglich, dünne Folien unter ca. 300 µm Dicke herzustellen.

Es wurde auch bereits vorgeschlagen (DE 197 50 846), eine Komponente aus Polyvinylacetat und Alkali-Wasserglas herzustellen, und diese Komponente zusammen mit Stärke und einem hydrophoben Polymer, zum Beispiel Polyvinylacetat, zu einem qualitativ hochwertigeren Polymergemisch zu extrudieren. Zur Herstellung der Komponente wurde Polyvinylacetat in Gegenwart katalytischer Zusätze von niedermolekularen, organischen Mono-, Di- und Trihydroxylverbindungen (z.B. Methanol, Ethanol, Ethylenglycol, Glyzerin) und unter kontinuierlicher Zugabe von basisch reagierenden Verbindungen und des Alkali-Silikats im Batch - Prozeß bis zu 90 % Hydrolisierungsgrad verseift.

Es hat sich gezeigt, daß mit dieser Komponente, die offensichtlich als Verträglichkeitsvermittler wirkt, Polymergemische mit hohen Stärkeanteilen analog zu DE 195 33 800 extrudiert werden können. Die aus diesen Polymergemischen hergestellten Produkte haben in mehreren Parametern eine deutlich höhere Qualität. Insbesondere können Folien mit einer Stärke von unter 100 µm hergestellt werden.

Ausgehend von den ökologischen Zielen, nachwachsende Rohstoffe noch stärker zu nutzen und umweltverträgliche Produkte wirtschaftlich herzustellen, ist es Aufgabe der Erfindung, ein Polymer-Blend auf Basis thermoplastischer Stärke mit verbesserten Eigenschaften zu schaffen.

Unter den erfindungsgemäßen Verarbeitungsbedingungen gelingt es, eine bikontinuierliche Phasenmorphologie des Systems einzustellen und stabil zu halten. Fig. 1 zeigt eine lichtmikroskopische Aufnahme (Phasenkontrastmikroskopie) eines erfindungsgemäß hergestellten TPS-Bionolle-Blends. Ersichtlich ist die Bikontinuität der dunklen und hellen Phase, die stabil erhalten bleibt.

Die bikontinuierliche Phasenmorphologie des erfindungsgemäßen Polymer-Blends besitzt eine breitere Vielfalt im Eigenschaftsprofil (z. Bsp. größere Anteile an Stärke, bessere Zugänglichkeit für den biologischen Abbau, Einstellung der Permeationseigenschaften) als Systeme mit Insel-/Matrix-Strukturen (siehe L. A. Utracki, *Polymer alloys and Blends: Thermodynamics and Rheology*, München, Wien, New York, Hanser Publishers 1989 bzw. *Handbuch der technischen Polymerchemie*, VCH Verlag Chemie, Weinheim, New York, Basel, Cambridge, Tokyo). Transparente Filme sind bei sehr feinen Dispersionen (Teilchendurchmesser < 100 nm) möglich, bei denen eine ausgedehnte Phasenseparation nicht stattfindet. Die bikontinuierliche Phasenstruktur hat auch den Vorteil, dass die hydrophoben Eigenschaften der synthetischen Polymerkomponente auch bei einem relativ geringen Anteil an der Gesamtmasse auf den Werkstoff insgesamt übertragen werden. Gleichzeitig bleiben aber auch die Eigenschaften der thermoplastischen Stärke, wie hohe mechanische Festigkeit, geringe Sauerstoffpermeabilität, schnelle biologische Abbaubarkeit erhalten.

Eine auf einen Hydrolysegrad von vorzugsweise 30 bis 55 % teilverseifte PVAc-Komponente hat ebenfalls einen signifikanten Einfluß auf die Phasenstabilität der Polymermischung. Insbesondere für die Herstellung dünner Folien sollte vorzugsweise eine wässrige PVAc-Dispersion mit NaOH bei 120 bis 140°C verseift und durch anschließendes Zentrifugieren unter weitgehendem Entfernen der Nebenprodukte auf eine Restfeuchte von 15 - 35 % eingestellt werden. Eine höhere Restfeuchte erhöht die Wasseraufnahme der Polymermischung.

Bei verschiedenen erfindungsgemäßen Polymermischungen (z. B. gemäß Beispiele 8 und 11 der am Ende der Ausführungsbeispiele beigelegten Tabelle) wurde ein MFI (melt flow index) von ca 5 G7 10 min bei einer Temperatur von 130°C und 5 kg

besondere Eigenschaften der hydrolysierten Komponente zurückgeführt werden muß, denn die Molmasse wird durch das Hinzufügen einer weiteren synthetischen Komponente, wie z. Bsp. Bionolle (aliphatischer Copolyester der Fa. Showa Denko, Poly(butylensuccinat-co-adipat)), nicht weiter erhöht (Wert 6). In der Kombination mit dem Verträglichkeitsvermittler können die oben genannten vorteilhaften Wirkungen des aciden Katalysators ohne Nachteile hinsichtlich eines zu starken Abbaus der Molmasse genutzt werden. Wie in den Beispielen noch gezeigt wird, haben die aus den Polymermischungen extrudierten Folien sehr gute Festigkeitswerte. Dabei ist aus dem Vergleich der Werte, insbesondere 2, 4 und 5, sogar ein synergistischer Effekt von acidem Katalysator und Verträglichkeitsvermittler erkennbar.

Als Polymerkomponente kommen verschiedene aliphatische Polyester, und deren Copolymere, Polyvinylacetat (PVAc) und deren Copolymere, Polyvinylalkohol (PVOH) und deren Copolymere, wasserfeste Stärke- und Cellulosederivate sowie andere, vorzugsweise biologisch abbaubare, synthetische Polymere zum Einsatz.

Offensichtlich ist auf die Kombination der Zusätze von acidem Katalysator und hydrolysierte PVAc-Komponente auch zurückzuführen, daß zum einen, wie in den Ausführungsbeispielen näher gezeigt, aus der Polymermischung sehr dünne Folien gezogen und zum anderen in den Mischungen für Spritzgußprodukte ein hoher Stärkeanteil eingearbeitet werden kann. Gut geeignete Spritzgußgranulat wurden aus 65 - 75 % Stärke, 5 - 10 % Verträglichkeitsvermittler, dem aciden Katalysator sowie Rest Bionolle hergestellt.

Die native Stärke, die hydrolysierte Komponente auf PVAc-Basis und der Katalysator können zu einer gut fließenden Pulvermischung vermengt werden. Es ist aber auch möglich, den Katalysator vermischt mit Glycerin oder einem anderen polyfunktionellen Alkohol flüssig zu dosieren.

Der Pulvermischung sollte zur Verbesserung ihrer Fließfähigkeit vorzugsweise ca. 1 % gefüllte Kieselsäure zugesetzt werden. Durch einen vorzugsweise Zusatz von ca. 1 % Stearinsäure zur Pulvermischung wird die Verarbeitbarkeit im Extruder verbessert.

Strangproben von etwa 2 cm Länge werden 24 h im Wasser bei Raumtemperatur gelagert, danach wird das Oberflächenwasser mit Filterpapier entfernt und die Proben zur Ermittlung des Wasseraufnahmevermögens (Quellbarkeit) ausgewogen. Diese Proben werden anschließend 8 h bei 90 °C im Wärmeschrank getrocknet und ausgewogen. Unter Berücksichtigung des Feuchtegehaltes der ursprünglichen Proben, der an gleichzeitig getrockneten, ungequollenen Vergleichsproben ermittelt wird, kann der Masseverlust und damit der in kaltem Wasser lösliche Produktanteil bestimmt werden.

Für die Zugprüfungen werden Probekörper in der Form eines Schulterstabes aus der Folie in Extrusionsrichtung ausgestanzt und 48 h in einer Atmosphäre, die sich in einem geschlossenen Gefäß oberhalb einer 80 %igen Glycerin/Wassermischung bei Raumtemperatur einstellt, konditioniert.

Die Zugprüfung erfolgt mit einer ZWICK - Universalprüfmaschine (ZWICKI 1120) entsprechend der DIN 53 455. Zur Auswertung werden die Zugspannung beim Bruch, die Bruchdehnung und der E-Modul genutzt.

Die hydrolysierte Komponente wird durch Verseifung einer wässrigen Polyvinylacetat-Dispersion mit NaOH bei 120 – 140°C hergestellt.

Der Mischung werden 12,5 % Glycerin, bezogen auf das Gesamtgewicht zugegeben. Die Prozentsätze der Komponente und von Bionolle sind in der nachfolgenden Tabelle enthalten. Die Angaben sind auf 100 Gew.-% der Mischung ohne Glycerin bezogen. Der Anteil der nativen Stärke errechnet sich aus der Differenz zu 100 % (ebenfalls ohne Glycerin).

Aus der Tabelle ist zu erkennen, daß Blasfolien mit geringer Dicke (ca. 30 µm) herstellbar sind. Bei allen Versuchen wurde festgestellt, daß die Verarbeitungseigenschaften wesentlich verbessert waren. Die mechanischen Eigenschaften der Folien, erhöhte Zugfestigkeit, Dehnbarkeit usw., sind deutlich verbessert.

WO 01/10949

PCT/DE00/02661

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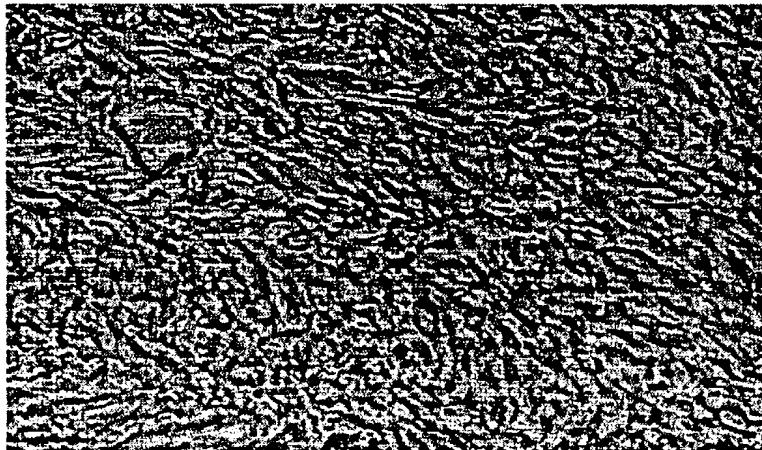


Fig. 1

**Patentansprüche**

1. Thermoplastisches Polymer-Blend mit einer bikontinuierlichen Phasenstruktur aus thermoplastischer Stärke, mindestens einem synthetischen Polymer und einer Hydrolysekomponente auf PVAc-Basis, wobei die Stärkekomponeute des Polymer-Blends ein gegenüber natürlicher Stärke nur geringfügig verringertes Molekulargewicht aufweist.
2. Thermoplastisches Polymer-Blend nach Anspruch 1, dadurch gekennzeichnet, daß es im weiteren Streckmittel, Füllstoffe, Gleitmittel, Fließmittel, Farbstoff, Pigmente oder Mischungen davon enthält.
3. Thermoplastisches Polymer-Blend nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß es bezogen auf die Gesamtzusammensetzung 30-70 Gew% thermoplastische Stärke, 20-40Gew% synthetisches Polymer und 6-25 Gew% Hydrolysekomponente auf PVAc-Basis und gegebenenfalls eine acide Katalysatorkomponente enthält.
4. Thermoplastisches Polymer-Blend nach Anspruch 1, wobei das synthetische Polymer ein biologisch abbaubarer aliphatischer Polyester oder deren Copolymeren oder Polyvinylacetat oder deren Copolymeren oder ein wasserfestes Stärkederivat oder Cellulosederivat oder Polyvinylalkohol oder deren Copolymeren oder ein wasserfestes Stärke- oder Cellulosederivat ist.
5. Verfahren zur Herstellung eines thermoplastischen Polymerblends durch reaktive Extrusion einer Mischung von nativer Stärke und wenigstens einem hydrophoben Polymer unter Zusatz einer hydrolysierten Komponente auf Polyvinylacetat-Basis und von niederen polyfunktionellen Alkoholen oder/und Wasser, dadurch gekennzeichnet, daß die Mischung in Gegenwart eines aciden Katalysators extrudiert wird.

6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß der acide Katalysator eine Organometallverbindung, wie Dibutylzinnoxid, Dibutylzinnlaurat, Tetra-2-ethylhexyltitanat, Triethanolaminzirkonat, mit Milchsäure chelatisierte Titanat-Verbindung, Triethanolamintitanat oder/und Alkyltitanate, ist.
7. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß der acide Katalysator eine Lewissäure (wie z. B. Triphenylphosphit) ist.
8. Verfahren nach Anspruch 6 oder 7, dadurch gekennzeichnet, daß die Mischung 0,5 bis 2 % des aciden Katalysators, bezogen auf ihr Gesamtgewicht, enthält.
9. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß der acide Katalysator eine Säure, wie Salpetersäure, Schwefelsäure, Salzsäure oder/und p-Toluolsulfonsäure, ist.
10. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß die Mischung 0,05 bis 0,2 % des aciden Katalysators, bezogen auf ihr Gesamtgewicht, enthält.
11. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß zur Herstellung der hydrolysierten Komponente das Polyvinylacetat auf einen Hydrolysegrad von 20 bis 70 % verseift wird.
12. Verfahren nach Anspruch 11, dadurch gekennzeichnet, daß das Polyvinylacetat auf einen Hydrolysegrad von 30 % bis 55 % verseift wird.
13. Verfahren nach Anspruch 11, dadurch gekennzeichnet, daß eine wäßrige Polyvinylacetat-Dispersion mit Natronlauge bei 120 - 140°C verseift wird.
14. Verfahren nach Anspruch 11, dadurch gekennzeichnet, daß die hydrolysierte Komponente auf Polyvinylacetat-Basis auf einen Restfeuchtegehalt von 15 - 35 % eingestellt wird.
15. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß die native Stärke, die hydrolysierte Komponente auf Polyvinylacetat-Basis und der Katalysator zu einer gut fließenden Pulvermischung vermengt werden.

(12) NACH DEM VERTRÄG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES  
PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

(19) Weltorganisation für geistiges Eigentum  
Internationales Büro



(43) Internationales Veröffentlichungsdatum  
15. Februar 2001 (15.02.2001)

PCT

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(81) Bestimmungsstaaten (national): **CN, JP, US.**

(84) Bestimmungsstaaten (regional): **europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).**

**Veröffentlicht:**

- *Mit internationalem Recherchenbericht.*
- *Vor Ablauf der für Änderungen der Ansprüche geltenden Frist; Veröffentlichung wird wiederholt, falls Änderungen eintreffen.*

*Zur Erklärung der Zweibuchstaben-Codes, und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.*

(54) **Title:** THERMOPLASTIC POLYMER BLEND PRODUCED FROM THERMOPLASTIC STARCH AND METHOD OF FOR THE PRODUCTION THEREOF

(54) **Bezeichnung:** THERMOPLASTICHE POLYMER-BLEND AUS THERMOPLASTICHER STÄRKE SOWIE VERFAHREN ZU DEREN HERSTELLUNG

(57) **Abstract:** The invention relates to a thermoplastic polymer blend with a bicontinuous phase structure produced from thermoplastic starch, at least from a synthetic polymer and a PVAc-based hydrolysis component, whereby the starch component of the polymer blended component in relation to natural starch has a lower molecular weight. The thermoplastic polymer blend is produced in such a way that a mixture of natural starch and at least one hydrophobic polymer with an admixture of hydrolysed polyvinyl acetate-based components are extruded, adding a low polyfunctional alcohol and /or water in the presence of an acidic catalyst. The thermoplastic polymer blend can be used to produce injection moulded, deep-drawn or blow-moulded parts, films and raw fibre materials as well as for melt film coatings.

(57) **Zusammenfassung:** Die Erfindung betrifft ein thermoplastisches Polymer-Blend mit einer bikontinuierlichen Phasenstruktur aus thermoplastischer Stärke, mindestens einem synthetischen Polymer und einer Hydrolysekomponente auf PVAc-Basis, bei dem die Stärkekomponente des Polymer-Blends ein gegenüber natürlicher Stärke nur geringfügig verringertes Molekulargewicht aufweist. Das thermoplastische Polymerblend wird erfahrungsgemäß so hergestellt, daß eine Mischung von nativer Stärke und wenigstens einem hydrophoben Polymer unter Zusatz einer hydrolysierten Komponente auf Polyvinylacetat-Basis und von niederen polyfunktionalen Alkoholen oder/und Wasser in Gegenwart eines aciden Katalysators extrudiert wird. Das thermoplastische Polymer-Blend kann für die Herstellung von Spritzguß-, Tiefzieh- oder Blasformteilen, Folien oder Faserrohstoffen sowie als Material für Schmelzebeschichtungen verwendet werden.

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Attorney Docket No. 266-01US**DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION (37 CFR 1.63)****As a below named inventor, I hereby declare that:**

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought of the invention entitled:

**Thermoplastic Polymer Blend Produced From Thermoplastic Starch and Method for the Production Thereof**

the specification of which

[ ] is attached hereto; or  
[X] was filed on 08/05/2000  
as US Application Ser. No.  
or PCT Application No. PCT/DE00/02661  
and was amended on \_\_\_\_\_.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56.

I hereby claim foreign priority benefits under Title 35 U.S.C. 119 (a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(b) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or any PCT international application having a filing date before that of the application on which priority is claimed:

Prior Foreign Application Ser. No.	Country	Foreign Filing Date (Month/Day/Year)	Priority Claimed	
			Yes	No
199 38 672.2	Germany	8/6/1999	X	

Attorney Docket No. 266-01US

I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States provisional application(s) listed below:

Application No.	Filing Date (Month/Day/Year)

I hereby claim the benefit under Title 35 U.S.C. 120 of any United States application(s), or 365(c) of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of 35 U.S.C. 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

U.S. Parent Application or PCT Parent No.	Parent Filing Date (Month/Day/Year)	Parent Patent No.

As a named inventor, I hereby appoint the following registered practitioner to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these

Attorney Docket No. 266-01US

statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Inventor's signature: \_\_\_\_\_ Date: \_\_\_\_\_

Residence:

Citizenship:

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Additional inventors are being named on the supplemental Additional Inventor(s) sheet(s)